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SURFACE TREATING AGENT FOR PAPER

Abstract:

[Matters to be Solved]

To provide a surface treating agent for paper suitable for recycling of damaged and used paper giving an excellent sizing effect to paper, significantly improving an aptitude to printing and being excellent in maceration property of paper.

[Solving Means]

A polyion complex substance comprising a graft starch polymer and an anionic polymer containing a hydrophobic group is applied on the surface of paper.

Claims:

1. A surface treating agent for paper, characterised in that, the agent is composed of a polyion complex of the following component (A) and component (B)

where a graft starch paper (A) which is prepared by polymerisation of a monomer mixture consisting of (meth)acrylamide (a1) and an anionic vinyl monomer (a2) as an essential component in an aqueous solution containing a

cationic starch and

an anionic copolymer (B) containing a hydrophobic group which is prepared by polymerisation of a monomer mixture consisting of a hydrophobic copolymer vinyl monomer (b1) and an anionic vinyl monomer (b2) as an essential component are main components.

2. The surface treating agent for paper according to claim 1, wherein the compounding ratio of the graft starch polymer (A) to the hydrophobic group-containing anionic copolymer (B) in terms of (A):(B) is from 70:30 to 30:70 parts by weight.

3. The surface treating agent for paper according to claim 1 or 2, wherein the graft starch polymer (A) is a graft starch polymer (A) which is prepared by polymerisation of 20-80% by weight of a vinyl monomer mixture consisting of 50-98 molar % of (meth)acrylamide (a1), 1-30 molar % of an anionic vinyl monomer (a2) and 1-20 molar % of a cationic vinyl monomer (a3) with an aqueous solution containing 20-80% by weight of a cationic starch.

4. The surface treating agent for paper according to any of claims 1, 2 and 3, wherein the cationic vinyl monomer (a3) in the graft starch polymer (A) is N,N-dialkylaminoalkyl (meth)acrylamide.

Detailed Description of the Invention:

[Technical Field of the Invention]

The present invention relates to a surface treating agent for paper and, more particularly, it relates to a surface treating agent for paper consisting of a polyion complex substance comprising a specific graft starch polymer and hydrophobic group-containing anionic copolymer. The present invention provides a surface treating agent for paper suitable for recycling of damaged and used paper giving an excellent sizing effect to paper, significantly improving an aptitude to printing and being excellent for maceration property of paper.

[Prior Art]

It is well known that, with regard to a surface treating agent for paper, there have been used oxidized starch, hydroxyethyl etherized starch,

thermochemically modified starch, polyvinyl alcohol, acrylamide type polymer, cellulose type polymer such as carboxymethylcellulose, styrene-maleic acid type copolymer, latex, vinyl acetate type polymer, etc. and, among them, oxidized starch, polyvinyl alcohol and acrylamide type polymer have been frequently used. However, in the case of an oxidized starch and polyvinyl alcohol, a cooking step is necessary in their use whereby there is a problem in their operation and, in addition, there are additional problems such as foaming and staining upon application and putrefaction of starch. On the other hand, an acrylamide type polymer has an excellent surface treating effect and its use tends to increase but, because of its high cost, its use is limited in view of economy. Further, the paper which is applied with the acrylamide type polymer has a tendency that maceration of damaged and used paper is deteriorated whereby that is a problem from a viewpoint of recycle of paper.

[Problems to be Solved by the Invention]

In recent years, there have been a demand that compounding rate of recycled paper is to be increased for the materials of paper due to environmental problems, that paper manufacturing machines are to be in a closed system due to restriction for waste water and that paper manufacturing machines are to be in high speed for improving the productivity. In addition, there are significant developments in printing technique and there have been a strong demand for improvement in aptitude of paper for printing and in surface strength of paper together with recent progresses in high printing speed, off-setting, water solubilization of gravure ink, multi-coloured printing, diversification of printing methods and high printing quality. Particularly with regard to a printing aptitude, there is a strong demand in an off-set printing for paper of a strong sizing corresponding to wetting water while, in an aqueous gravure printing, there is a strong demand for improvement in colouring of ink in the printing caused by permeability of aqueous gravure ink.

In order to solve the above-mentioned problems, the present inventors have carried out intensive studies for providing a surface treating agent for paper suitable for recycling of damaged and used paper giving an excellent sizing effect to paper, significantly improving an aptitude to printing and being excellent for maceration property of paper and, as a result, they have accomplished the present invention which will be mentioned hereinafter.

[Means for Solving the Problems]

Thus, the present invention relates to a surface treating agent for paper, characterised in that, the agent is composed of a polyion complex of the following component (A) and component (B)

where a graft starch paper (A) which is prepared by polymerisation of a monomer mixture consisting of (meth)acrylamide (a1) and an anionic vinyl monomer (a2) as an essential component in an aqueous solution containing a cationic starch and

an anionic copolymer (B) containing a hydrophobic group which is prepared by polymerisation of a monomer mixture consisting of a hydrophobic copolymer vinyl monomer (b1) and an anionic vinyl monomer (b2) as an essential component

are main components.

[Embodiments of the Invention]

The present invention will now be further illustrated as hereunder. A cationic starch used for the graft starch polymer (A) of the present invention is that where a cationic group is introduced according to a conventional method into starch and/or modified starch. To be more specific, a cationic group is introduced into various kinds of starch where maize, wheat, potato, tapioca, rice, etc. are used as a material and a modified product thereof and one or more kind(s) of them is/are used.

With regard to a viscosity of the cationic starch used in the present invention, the range of 50-1,000 cps (30°C) at the concentration of 30% is preferred.

In the preparation of the cationic starch, starch and/or modified starch are/is made contained with at least one kind of basic nitrogen selected from primary, secondary and tertiary amino groups and a quaternary ammonium group. The amount of the basic nitrogen contained therein is preferably 0.1% by weight or more. To be more specific, starch and/or modified starch may be made to react with a cationizing agent consisting of a reaction product of dialkylamine or trialkylamine with epichlorohydrin.

Particularly preferred one is a product having a low viscosity which is prepared by cationization of modified starch decomposed by the above-mentioned various types of starch with an enzyme such as amylase and/or prepared by decomposition of cationic starch (manufactured by cationization

of starch and/or modified starch using a cationizing agent) with an enzyme such as amylase.

The (meth)acrylamide (a1) used in the graft starch polymer (A) in the present invention includes acrylamide and methacrylamide and any of them may be used solely or both may be used jointly.

Examples of the anionic vinyl monomer (a2) used in the graft starch polymer (A) are acrylic acid, methacrylic acid, itaconic acid, maleic acid anhydride, fumaric acid, vinylsulphonic acid, 2-acrylamido-2-methylpropanesulphonic acid and salts thereof with sodium, potassium or ammonium. One of them may be used solely or two or more thereof may be used jointly.

Examples of the cationic vinyl monomer (a3) used in the graft starch polymer (A) of the present invention are N,N-dialkylaminoalkyl (meth)acrylate such as N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate and N,N-dimethylaminopropyl (meth)acrylate; N,N-dialkylaminoalkyl (meth)acrylamide such as N,N-dimethylaminoethyl (meth)acrylamide and N,N-dimethylaminopropyl (meth)acrylamide; vinyl monomer having a tertiary amino group such as vinylpyridine, vinylimidazole, allylamine and diallylamine; and hydrochloride, sulphate, formate, acetate and sulphamate thereof. Further examples are quaternary ammonium salt prepared by the reaction of a vinyl monomer having a tertiary amino group with a quaternizing agent such as alkyl halide (e.g. methyl chloride), arylalkyl halide, dimethyl sulphate, diethyl sulphate, epichlorohydrin, 3-chloro-2-hydroxypropyltrimethylammonium chloride and glycidylalkylammonium chloride. One of them may be used solely or two or more of them may be used jointly. Dialkylaminoalkyl (meth)acrylamide or a salt thereof is particularly preferred since, when it is made into a polyion complex substance, stability of the product with a lapse of time is excellent.

Incidentally, the graft starch polymer of the present invention may contain another vinyl monomer which is copolymerisable with the (meth)acrylamide (a1), the anionic vinyl monomer (a2) and the cationic vinyl monomer (a3) within an extent of not more than 10 molar %. Examples of such a monomer are methylol (meth)acrylamide, dimethyl acrylamide, bifunctional, trifunctional and tetrafunctional cross-linking vinyl monomers, diisopropyl acrylamide, (meth)acryl esters, acrylonitrile, vinyl acetate, hydroxy-containing (meth)acrylic acid, esters and vinylpyrrolidone.

Manufacture of the graft starch polymer (A) in accordance with the present invention may be carried out by a conventional method. For example, an aqueous solution of the above-mentioned cationic starch, the above-mentioned monomer components (a1), (a2) and (a3) and water are charged in a reactor equipped with a nitrogen gas inlet and a stirrer and made to react at the reaction temperature of 40-80°C for 1-5 hour(s) using a polymerisation initiator such as a peroxide (e.g., hydrogen peroxide, ammonium persulphate, potassium persulphate or ammonium hydroperoxide), a redox initiator where such a peroxide is combined with a reducing agent such as bisulphite and a water-soluble azo type polymerisation initiator whereupon the desired graft starch polymer (A) can be prepared.

In the manufacture of a graft starch polymer (A) in the present invention, it is preferred that, in an aqueous solution containing 20-80 parts by weight of a cationic starch, a monomer mixture consisting of 50-99 molar % of (meth)acrylamide (a1), 1-30 molar % of anionic vinyl monomer (a2) and 1-20 molar % of cationic vinyl monomer (a3) is polymerised therewith. When the cationic starch is less than 20 parts by weight, there is a problem in terms of maceration of the paper while, when it is more than 80 parts by weight, the printing aptitude is a bit poor.

Examples of the hydrophobic vinyl monomer (b1) used in a hydrophobic group-containing anionic copolymer (B) in the present invention are α,β -unsaturated polybasic acid alkyl (half) esters including styrene, alkylstyrene, alkyl (meth)acrylate, vinyl acetate, olefins and maleic acid anhydride. One of them may be used solely or two or more thereof may be used jointly.

Examples of the anionic vinyl monomer (b2) used in the hydrophobic group-containing anionic copolymer (B) in the present invention are acrylic acid, methacrylic acid, itaconic acid, maleic acid anhydride, maleic acid, fumaric acid, vinylsulphonic acid, styrenesulphonic acid, 2-acrylamido-2-methylpropanesulphonic acid, etc. and salts thereof with sodium, potassium, ammonium, etc. One of them may be used solely or two or more thereof may be used jointly.

There is no problem at all to use other monomer components such as vinyl chloride, vinylidene chloride, acrylamide and derivatives thereof, vinylpyrrolidone, allyl alcohol, acrylonitrile and various other monomers so far as they do not deteriorate the advantage of the present invention.

With regard to the hydrophobic group-containing anionic copolymer (B), the preferred ones are salt of a styrene-maleic acid type copolymer, salt of a styrene-(meth)acrylate-(meth)acrylic acid type copolymer, salt of a copolymer of olefin with maleic acid anhydride and partial ester or partial amide thereof and salt of a vinyl acetate-maleic acid type copolymer.

The above-mentioned salt of a styrene-maleic acid type copolymer is a salt of a copolymer of styrene with maleic acid anhydride or a salt of a copolymer of styrene with maleate. The said maleate is a half ester comprising maleic acid anhydride with a C_{1-30} linear or branched alkyl alcohol or alkylphenylalcohol and, depending upon the desired physical property, one of them may be used solely or two or more thereof may be used jointly. The composition ratio for copolymerisation of styrene with maleic acid anhydride or with maleic acid half ester is usually in an equimolar ratio although there is no problem even when the amount of one of them is more than that of another.

With regard to the above-mentioned salt of styrene-(meth)acrylic acid copolymer, the copolymer is prepared by copolymerisation of styrene with acrylic acid, styrene with methacrylic acid or styrene with acrylic acid and methacrylic acid. The composition ratio of the styrene to (meth)acrylic acid is 30-90 molar % of styrene to 10-70 molar % of (meth)acrylic acid or, preferably, 40-60 molar of styrene to 40-60 molar % of (meth)acrylic acid.

With regard to the above-mentioned salt of styrene-(meth)acrylate-(meth)acrylic acid copolymer, the copolymer is prepared by copolymerisation of styrene with (meth)acrylate and (meth)acrylic acid. The preferred composition ratio is 0-20 molar % of styrene, 30-90 molar % of (meth)acrylate and 10-70 molar % of (meth)acrylic acid.

With regard to the above-mentioned olefin-maleic acid anhydride copolymer, the preferred composition ratio is 40-60 molar % of ethylene, diisobutylene and α -olefin and 40-60 molar % of maleic acid anhydride. Incidentally, it is also possible to use a partial alcohol ester or a partial amide of the copolymer.

Manufacture of the hydrophobic group-containing anionic copolymer (B) in the present invention may be carried out by means of a solution polymerisation, a bulk polymerisation, an emulsion polymerisation, etc. according to a conventional method and, among them, a solution

polymerisation is preferred. Examples of the catalyst for the polymerisation are a peroxide such as benzoyl peroxide and an azo compound such as azobisisobutyronitrile. The copolymer after the copolymerisation is neutralised with an alkali such as an alkaline metal (e.g., sodium hydroxide and potassium hydroxide), ammonium, alkylamine, alkanolamine, morpholine compounds, polyvalent amines (e.g., ethylenediamine), etc. to form a salt whereupon an aqueous solution of the hydrophobic group-containing anionic copolymer (B) is prepared. The above-mentioned alkaline substances may be used either solely or jointly. Degree of neutralisation is 50-120 molar % or, preferably, 90-100 molar %.

Molecular weight of the hydrophobic group-containing anionic copolymer (B) of the present invention is about 2,000-200,000 or, preferably, 5,000-100,000. When the molecular weight is too low, a sufficient sizing effect is not achieved while, when it is more than 200,000, viscosity becomes high whereby a working ability becomes bad.

The aqueous solution of the hydrophobic group-containing anionic copolymer (B) of the present invention may be, if necessary, further compounded with a water-soluble solvent such as alcohol, glycol or Cellosolve with an object of stabilisation of viscosity and improvement in volatility.

The compounding ratio of the graft starch polymer (A) to the hydrophobic group-containing anionic copolymer (B) in the present invention in terms of (A):(B) is from 70:30 to 30:70. When the amount of the graft starch polymer is less than 30 parts by weight, there are problems in the printing aptitude and maceration property while, when it is more than 70 parts by weight, a sizing effect of paper is deteriorated.

With regard to the polyion complex substance of the graft starch polymer (A) with the hydrophobic group-containing anionic copolymer (B) in the present invention, it is necessary that both components are previously mixed to prepare a mixture of a single type. Since a balance changes depending upon the pH of the said mixture, an organic acid, an inorganic acid or an alkali is used for adjusting to an appropriate pH whereby no precipitate is formed depending upon their mixing ratio or ionic ratio.

The ion complex substance of the present invention is a complex which is prepared by the reaction of an amphoteric graft starch polymer (A) (high-molecular electrolyte) having a positive charge with an hydrophobic group-

containing anionic copolymer (B) (high-molecular electrolyte) having a negative charge. It is believed that, as a result of formation of the polyion complex substance consisting of the component (A) having the above-mentioned surface strength and printing aptitude and the component (B) having the above-mentioned sizing property, the same form as in a high-molecular polymer is produced and a strong coat is formed on the surface of the paper whereby an object of the present invention is achieved.

Concentration of the surface treating agent of the present invention applied to paper is determined depending upon the absorbed amount to the paper (adhered amount) and upon the quality requested to the paper and, usually, the solid content is 0.5-10% by weight and the applying amount is 0.01-5 g/m².

The applying solution containing the surface treating agent according to the present invention may be applied on the surface of the paper by various applying means such as size press, gate roll, calendar, air knife coater, blade coater, etc. according to a conventional method. Incidentally, a spraying method or an impregnation method may be used if necessary.

In the surface treating agent of the present invention, a polyion complex substance consisting of the graft starch polymer (A) and the hydrophobic group-containing anionic copolymer (B) is an essential component but, so far as the advantage of the component is not deteriorated, other compounding agents such as starch derivatives, water-soluble cellulose derivatives, polyvinyl alcohol, vegetable gum substances, alginate, polymers of an acrylamide type, etc. may be further compounded therewith.

There is no particular limitation for the paper to which the surface treating agent of the present invention is applied and there is no limitation for pulp, filler, internally added sizing agent, paper reinforcing agent, fixing agent, etc. used therefor. It is also possible to use various kinds of paper from neutrally manufactured to acidically manufactured ones. Examples of the applicable paper are high quality paper, medium quality paper, paper for newspaper, coated paper, special paper, processed paper, liner, original paper for cores, paper for PPC, paper for ink jet or toner printers, heat sensitive paper and other paper for information recording, original paper for gypsum board and paper for building materials.

[Examples]

Now the present invention will be further illustrated by way of the following Examples, Comparative Examples and Referential Examples although the present invention is not limited thereto.

Example 1.

Cationic tapioca starch (concentration: 20% aqueous solution; viscosity: 100 cps at 25°C; degree of substitution (DS): 0.05) (190 parts), 80 parts of 40% acrylamide, 1.2 parts of 80% acrylic acid and 4.5 parts of dimethylaminopropyl acrylamide were mixed, water was added to make 440 parts and pH was adjusted to 5.0 by addition of 10% by weight of potassium hydroxide. Whole amount of the mixture was charged in a flask equipped with a stirrer and heated, each 0.5 part of ammonium persulphate and sodium bisulphite was added when the inner temperature was 55°C, the mixture was polymerised at 65-70°C for 3 hours and cooled and water was added to make the total volume 60 parts to give an aqueous solution of a graft starch polymer (A-1) having a viscosity of 2,500 cps (at 25°) and a solid content of 15%. On the other hand, 50 parts by weight of styrene and 50 parts by weight of methacrylic acid were subjected to a solution polymerisation under refluxing in the presence of an isopropyl alcohol solvent using azobisisobutyronitrile (AIBN) as an initiator and, after the polymerisation, an appropriate amount of aqueous ammonium was added to neutralise. After that, the solvent was removed by means of a vacuum distillation and an appropriate amount of water was added to give an aqueous solution of a hydrophobic group-containing anionic copolymer (B-1) having a viscosity of 80 cps (at 25°C), a solid content of 15% and a pH of 9.0. The above-prepared both aqueous solutions were mixed to give a surface treating agent consisting of a polyion complex substance of the component (A-1) and the component (B-1). Its properties are shown in Table 1.

Examples 2-4.

The same operation as in Example 1 was carried out except that appropriate changes were made as mentioned in Table 1 for the type and the amount of cationic starch, acrylamide (a1), anionic vinyl monomer (a2), cationic vinyl monomer (a3) and other monomers in the graft starch polymer (A); the type and the amount of hydrophilic group-containing vinyl monomer (b1) and anionic vinyl monomer (b2) in the hydrophobic group-containing anionic

copolymer (B); and the ratio by weight of the graft starch polymer (A) to the hydrophobic group-containing anionic copolymer (B) whereupon the surface treating agents of Examples 2-7 and Comparative Examples 1-4 were prepared. Their properties are shown in Table 1.

Table 1

| Ex. | | Graft Starch Polymer (A) | | | | | | |
|-------------|---|--------------------------|--------------------|------------------------|--------|-----------|-----------|----------------|
| | | Type | CS(a) Type | Monomer Components (a) | | | | CS/ Monomer |
| | | | | (a1) | (a2) | (a3) | Others | |
| Ex. | 1 | A-1 | Tapioca DS:0.05 | AAM 91 | AA 3 | DMA PAA 6 | - | 50/50 |
| | 2 | A-1 | " | " | " | " | - | 50/50 |
| | 3 | A-1 | " | " | " | " | - | 50/50 |
| | 4 | A-2 | " | AAM 93.5 | TA 1.5 | DMA PAA 5 | - | 70/30 |
| | 5 | A-4 | " | AAM 90.99 | AA 3 | DMA PAA 6 | MBAA 0.01 | 50/50 |
| | 6 | A-5 | Potato DS:0.15 | AAM 91 | AA 3 | DMA PAA 6 | - | 50/50 |
| | 7 | A-6 | Maize DS:0.1 | AAM 92.5 | IA 1.5 | DMA PAA 6 | - | 50/50 |
| Comp Ex. | 1 | C-1 | - | AAM 91 | AA 3 | DMA PAA 6 | - | 0/100 |
| | 2 | A-1 | Tapioca DS:1.05 | AAM 91 | AA 3 | DMA PAA 6 | - | 50/50 |
| | 3 | - | - | - | - | - | - | - |
| | 4 | A-2 | - | AAM 90 | AA 10 | - | - | 0/100 |

(continued

Table 1 (continued)

| | | Hydrophobic Group-Containing Anionic Copolymer (B) | | | Ratio of (A) or (C)/(B) | pH | Solid Content | Viscosity |
|---------|---|--|-----------------------|--------|-------------------------|-----------------|---------------|-------------|
| | | Type | Monomer Component (b) | | | 10-fold diluted | % | cps at 25°C |
| | | | (b1) | (b2) | | | | |
| Ex | 1 | B-1 | St 50 | MAA 50 | 70/30 | 7.2 | 15 | 2300 |
| | 2 | " | " | " | 50/50 | 8.2 | 15 | 1700 |
| | 3 | " | " | " | 30/70 | 8.6 | 15 | 500 |
| | 4 | " | " | " | 70/30 | 7.4 | 15 | 3000 |
| | 5 | " | " | " | " | 8.3 | 15 | 2100 |
| | 6 | B-2 | St 70 | AA 30 | " | 8.2 | 15 | 1900 |
| | 7 | B-2 | " | " | " | 8.3 | 15 | 2200 |
| Comp Ex | 1 | B-1 | St 50 | MAA 50 | 70/30 | 8.3 | 15 | 2100 |
| | 2 | - | - | - | - | 4.2 | 15 | 2500 |
| | 3 | B-1 | St 50 | MAA 50 | 0/100 | 9.0 | 15 | 80 |
| | 4 | " | " | " | 70/30 | 8.8 | 15 | 1500 |

Abbreviations in Table 1 are as follows.

CS: cationic starch
AAM: acrylamide
AA: acrylic acid
IA: itaconic acid
DMAPAA: N,N-dimethylaminopropyl acrylamide
MBAA: methylenebisacrylamide

Evaluation of the properties of the surface treating agents.

Properties of the surface treating agents of the above-mentioned Examples 1-7 and Comparative Examples 1-4 and also of Referential Examples 1-2 were evaluated.

(1) Paper to which the surface treating agent is applied

. unapplied white liner 180 g/m²
. unapplied high-quality paper 60 g/m²

(2) Method of surface application

(a) Evaluation for the liner

An applying solution in which the adhered amount of the surface treating agent of each of Examples 1-7, Comparative Examples 1-4 and Referential Examples 1-2 was made 0.3 g/m² (in terms of solid) by diluting with water was applied on both surfaces of white liner using a roll coater and dried at 90°C using a rotary drier for 1 minute to conduct a surface application. Applied amount of the surface treating agent and quality of the paper are shown in Table 2.

Table 2

| Surface Treating Agent | Applied Amount (g/m ²) | Colouration of Aqueous Gravure Ink (Gloss) | IGT Test (cm/s) | RT Test | Cob Test (sec) |
|------------------------|------------------------------------|--|-----------------|---------|----------------|
| Example 1 | 0.312 | 7 | 263 | 5 | 26.0 |
| 2 | 0.322 | 8 | 250 | 4 | 23.2 |
| 3 | 0.309 | 7 | 223 | 3 | 21.6 |
| 4 | 0.320 | 7 | 240 | 3~4 | 25.8 |
| 5 | 0.329 | 8 | 273 | 5 | 23.2 |

| | | | | | |
|-----------|-------|---|-----|---|------|
| 6 | 0.311 | 7 | 266 | 5 | 24.5 |
| 7 | 0.326 | 7 | 259 | 5 | 24.8 |
| Comp.Ex.1 | 0.319 | 7 | 250 | 4 | 28.3 |
| 2 | 0.301 | 1 | 200 | 3 | 39.2 |
| 3 | 0.362 | 2 | 158 | 1 | 26.3 |
| 4 | 0.319 | 3 | 190 | 2 | 30.2 |
| Ref.Ex. 1 | 0.320 | 1 | 180 | 3 | 38.6 |
| 2 | 0.316 | 6 | 210 | 3 | 35.7 |

Referential Example 1: Oxidized starch (MS-3800 manufactured by Nippon Shokuhin Kako KK)

Referential Example 2: Polyvinyl alcohol (PVA-117 manufactured by Kuraray)

(b) Evaluation for the high-quality paper

An applying solution in which the adhered amount of the surface treating agent of each of Examples 1-7, Comparative Examples 1-4 and Referential Examples 1-2 was made 0.2 g/m² (in terms of solid) by diluting with water was applied on both surfaces of high-quality paper using a roll coater and dried at 90°C using a rotary drier for 1 minute to conduct a surface application. Applied amount of the surface treating agent and quality of the paper are shown in Table 3.

Table 3

| Surface Treating Agent | Applied Amount (g/m ²) | Stöchigt Method (sec) | IGT Test (cm/s) | RI Test | Maceration Test |
|------------------------|------------------------------------|-----------------------|-----------------|---------|-----------------|
| Example 1 | 0.219 | 18.2 | 176 | 5 | 3~4 |
| 2 | 0.218 | 20.3 | 159 | 4 | 4 |
| 3 | 0.226 | 22.4 | 110 | 2~3 | 4 |
| 4 | 0.219 | 18.9 | 145 | 3~4 | 5 |
| 5 | 0.223 | 18.4 | 185 | 5 | 4 |
| 6 | 0.216 | 17.9 | 175 | 4~5 | 4 |
| 7 | 0.229 | 17.6 | 165 | 4 | 4 |
| Comp.Ex.1 | 0.215 | 15.4 | 160 | 4 | 1 |
| 2 | 0.226 | 4.5 | 104 | 2 | 5 |
| 3 | 0.230 | 16.2 | 80 | 1 | 2~3 |
| 4 | 0.216 | 12.5 | 103 | 2 | 2~3 |
| Ref.Ex. 1 | 0.230 | 5.0 | 96 | 2 | 5 |
| 2 | 0.228 | 8.2 | 135 | 3 | 3 |

Referential Example 1: Oxidized starch (MS-3800 manufactured by Nippon Shokuhin Kako KK)

Referential Example 2: Polyvinyl alcohol (PVA-117 manufactured by Kuraray)

(3) Method of evaluation of paper quality by surface treating agent

(a) Sizing effect: Stöchigt method (JIS P-8122-1976)
Cob water absorption method (JIS P-8140)

(b) Printing aptitude test:

. IGT Test: Printing was carried out using an IGT printing tester and expressed in terms of acceleration to cause a picking.

Tester used: IGT printing aptitude tester manufactured by Kumagaya Riki Kogyo KK

Ink used: Black ink TV 15 manufactured by Toyo Ink KK

Conditions: Printing pressure: 50 kg/m²; tension A

. RI Test: Printing test was carried out using an RI tester (manufactured by Akira Seisakusho) and the state of picking was evaluated in five stages of from 5 (excellent) to 1 (bad).

. Colouring test of aqueous gravure printing: Aqueous gravure ink was applied using a bar coater (No. 1) onto a paper which was applied with the surface treating agent and, after a natural drying, gloss of the ink was measured by a gloss-meter (Horiba TG 310).

(c) Maceration test: Paper (1 g) where the surface was treated was and cut into a size of 5 × 5 mm was placed into 100 g of water of 30°C and macerated by stirring for 5 minutes using a high-speed stirrer (2,000 rpm). The slurry after the maceration was made into paper by hand and the macerated state was evaluated in five stages of from 5 (excellent) to 1 (bad).

[Advantage of the Invention]

The surface treating agent according to the present invention consists of a polyion complex substance comprising a graft starch polymer (A) and a hydrophobic group-containing anionic copolymer (B) and used in various size

press, gate roll, calendar application, etc. in the manufacture of paper whereupon it gives a strong sizing effect, significantly improves the printing aptitude and is excellent in maceration property of paper whereby it is suitable for recycling of damaged and used paper.

[End]

